Development of Composite Nonlinear Optical Materials Based on Local Field Enhancement

Final Report

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This research project has been directed toward the development of nonlinear optical materials with properties enhanced by local field effects. Our investigations of these issues have been broadly based, ranging from fundamental studies of local field effects in atomic vapors to engineering studies of nonlinear optical and electrooptic materials with local-field enhanced response.

Historical Background. Local field effects are often encountered in the context of the Lorentz-Lorenz or Clausius-Mossotti relations. These relations stem from the realization, often ascribed to Lorentz [1], that the electric field that acts on an individual molecule in a material system is not the macroscopic electric field E but rather is a corrected, or local, field

$$E_{loc} = E + \frac{4\pi}{3}P, \tag{1}$$

where P is the polarization, that is, the dipole moment per unit volume. On the basis of this assumption, and on performing a volume average of the electronic response of the material system, one finds that the dielectric constant of the material obeys the relation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3}N\alpha, \tag{2}$$

where N is the molecular number density and α is the molecular polarizability. This relation can be expressed equivalently as $\epsilon = 1 + 4\pi L N\alpha$, where L is the local field correction factor given by

$$L = \frac{1}{1 - \frac{4\pi}{3}N\alpha} = \frac{\epsilon + 2}{3}. \tag{3}$$

This model can be extended to the nonlinear optical response [2, 3]. One finds, for example, that

$$\chi^{(3)}(\omega_4, \omega_3, \omega_2, \omega_1) = L(\omega_4)L(\omega_3)L(\omega_2)L(\omega_1)N\gamma, \tag{4}$$

where γ is the second hyperpolarizability. Note that the local field correction factor appears to fourth order in this expression. Since this correction factor appears to high order, one expects that the enhancement of the nonlinear response can become large. In the theory of composite

materials, which is summarized below, one finds that the effective nonlinear susceptibility has a form analogous to that of Eq. (4) where the local field factor now provide a measure of how the electric field in a given component of the composite is related to the spatially averaged electric field. But the same conclusion still holds: local field effects play a crucial role in establishing the strength of the nonlinear optical response.

Measurements of Local Field Effects in Atomic Vapors. We have conducted experimental studies of the influence of local field effects on the linear and nonlinear optical response of a dense atomic vapor. The motivation of this study was to verify the validity of standard theoretical models of local field effects, such as those described above, before making use of these models for the design of composite nonlinear optical materials. In the course of this study, we performed [4] the first accurate experimental measurement of the Lorentz red shift, an effect predicted [1] by Lorentz in the nineteenth century and which is a direct consequence of local field effects.

To understand the origin of the Lorentz red shift, let us assume that the atomic polarizability is given by the standard expression

$$\alpha = \frac{f r_e \lambda_0 c/4\pi}{\omega_0 - \omega - i(\Gamma/2)} \tag{5}$$

where f is the oscillator strength of the atomic transition, $r_e = e^2/mc^2$ is the classical electron radius, $\omega_0 = 2\pi c/\lambda_0$ is the transition frequency, and Γ is the transition damping rate. If this expression is introduced into Eq. (2), one finds that the dielectric constant can be expressed as

$$\epsilon = 1 + \frac{f r_e \lambda_0 c N}{\omega_0 - \Delta\omega_L - \omega - i(\Gamma/2)} \tag{6}$$

where $\Delta\omega_L = (1/3) f r_e \lambda_0 c N$ represents the Lorentz red shift, that is, the density-dependent frequency shift between the atomic polarizability (a microscopic quantity) and the dielectric constant (a macroscopic quantity).

To study these effects experimentally, we measured the optical properties of a potassium vapor as a function of atomic number density N. Because of the large absorption of a high-density atomic vapor near resonance, our technique entailed measuring the reflectivity of the interface between the potassium vapor and a sapphire window as a function of the laser frequency for various atomic number densities. Some of our results are shown in Fig. 1. We see that the curves shift to lower frequencies as the number density is increased from 1×10^{16} to 1.5×10^{17} atoms/cm^3. We also see that the experimental results are in good agreement with the predictions of a theoretical model based on Eq. (6) which also includes the influence of collisions and Doppler broadening.

Composite nonlinear optical materials. Much of our research has been aimed at obtaining an understanding of the physical processes that determine the linear and nonlinear optical

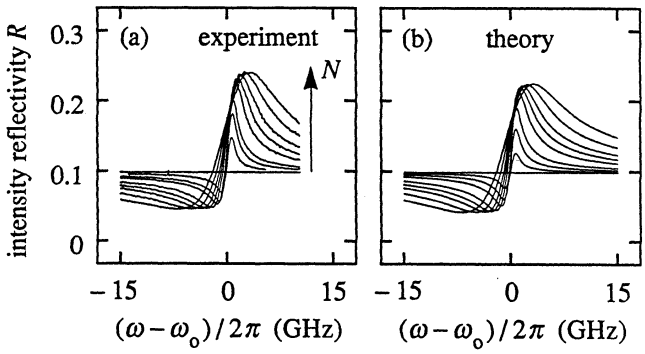

Figure 1: Measurement of the Lorentz red shift.

properties of nanocomposite materials. A significant accomplishment of this research, which is described in detail below, is the prediction and experimental verification that under proper conditions two materials can be combined in such a manner that the nonlinear susceptibility of the composite exceeds those of the constituent materials. This section also presents a survey of various geometrical structures of composite materials.

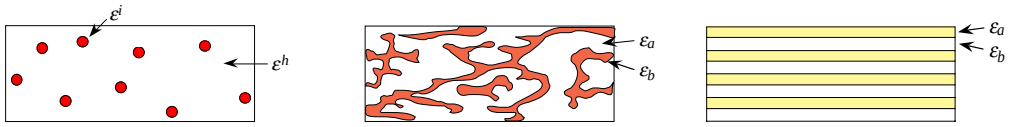

Figure 2: Composite material structures for use in nonlinear optics.

Some of the commonly encountered structures [5] of composite materials are shown in Fig. 2. The Maxwell Garnett [6] geometry consists of small inclusion particles embedded in a host material. The Bruggeman [7] geometry consists of two intermixed components. A composite geometry which is particularly well suited to careful characterization is that of alternating layers of two dissimilar materials [8]. In all the structures shown in Fig. 2, we assume that the two materials are intermixed on a distance scale much smaller than that of an optical wavelength. Under these conditions, the propagation of light can be describe by effective values of the optical constants that are obtained by performing a suitable volume average of the local optical response of the material. In fact, performing such an average can be rather subtle for situations involving the nonlinear optical response, because it is the nonlinear polarization that must be averaged, and the nonlinear polarization depends on the spatially inhomogeneous electric field amplitude in the composite material. The results of some of these calculations are described below. We do, however, make the assumption that the spatial extent of each region

is sufficiently large that we can describe its response using macroscopic concepts such as susceptibilities rather than using microscopic concepts such as polarizabilities. Roughly speaking, this assumption requires that many molecules be contained in even the smallest region of each component.

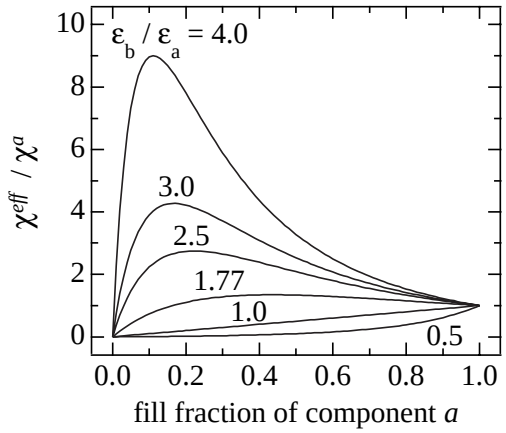

Figure 3: Predicted enhancement of the nonlinear optical susceptibility for a layered-geometry composite.

Layered Geometry Composites. We have performed theoretical [8] and experimental [9, 10, 11] studies of the nonlinear optical response of composite optical materials possessing a layered structure. Materials of this sort are inherently anisotropic. For light polarized parallel to the layers of the structure, we find that both the linear and nonlinear optical susceptibilities are given by simple volume averages of the properties of the constituent materials, that is, $\epsilon_{\text{eff}} = f_a\epsilon_a + f_b\epsilon_b$ and $\chi^{(3)}_{\text{eff}} = f_a\chi^{(3)}_a + f_b\chi^{(3)}_b$. Here f_a and f_b denote the volume fill fractions of components a and b, respectively. However, for light polarized perpendicular to the plane of the layers the linear dielectric constant is given by $1/\epsilon_{\text{eff}} = f_a/\epsilon_a + f_b/\epsilon_b$ and the third order susceptibility is given by

$$\chi^{(3)}_{\text{eff}} = \left|\frac{\epsilon_{\text{eff}}}{\epsilon_a}\right|^2 \left(\frac{\epsilon_{\text{eff}}}{\epsilon_a}\right)^2 f_a\chi^{(3)}_a + \left|\frac{\epsilon_{\text{eff}}}{\epsilon_b}\right|^2 \left(\frac{\epsilon_{\text{eff}}}{\epsilon_b}\right)^2 f_b\chi^{(3)}_b \tag{7}$$

Note that the factor $\epsilon_{\text{eff}}/\epsilon_a$ can be interpreted as a local field correction factor for component a. Eq. (7) predicts that under proper conditions a layered composite material can display enhanced response. Such results are illustrated in Fig. 3, under the assumption that only component a of the composite displays a nonlinear response. We see that the enhancement in the nonlinear susceptibility can be as large as a factor of 9 if the two constituents differ by a factor of 2 in their linear refractive indices. A smaller enhancement is predicted if the refractive indices of the two materials differ by a smaller factor. For example, the curve labeled

1.77 corresponds to the conditions of our initial experimental study of these effects, and it predicts an enhancement of 35%.

The experimental system which we used to first verify [9] these predictions consists of alternating layers of the conjugated polymer PBZT and of titanium dioxide. Layers were spin coated with a thickness of approximately 50 nm and were cured at elevated temperatures after each deposition. After curing, the PBZT has a refractive index of 1.65 and the titanium dioxide has a refractive index of 2.2. The third-order susceptibility of PBZT is several orders of magnitude larger than that of titanium dioxide, and is responsible for essentially the entire measured nonlinear response of the composite material. Since the more nonlinear constituent of the composite has the smaller linear refractive index, this composite structure is predicted to possess enhanced nonlinear response.

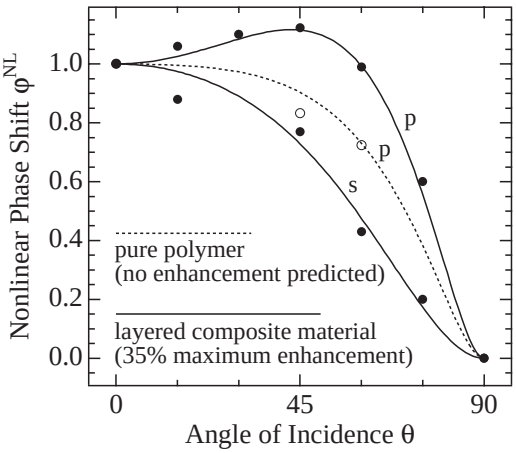

Figure 4: Measurement of enhanced nonlinear optical response of a composite nonlinear optical material.

These samples were studied experimentally by measuring the nonlinear refractive index experienced by an intense light beam. Some of our results [9] are shown in Fig. 4. Our experimental procedure involves measuring as a function of the angle of incidence the nonlinear phase shift experienced by the incident light beam. The phase shift was measured using the induced focusing (also known as z-scan) technique. For s polarized light, the measured phase shift was found to decrease uniformly with the angle of incidence. This behavior occurs because the light intensity inside the material decreases with increasing angle of incidence because of Fresnel reflection losses. An enhancement of the nonlinear response is predicted only for p polarized light, because in this case the electric field of the incident light wave has a component perpendicular to the planes of the layers of the composite. For p polarized light, we find that the measured nonlinear phase shift first increases with increasing angles of incidence and begins to decrease only for larger values of the incidence angle. These results are in

quantitative agreement with the the theoretical prediction that effective nonlinear susceptibility of the composite material for p polarized light is 35 % larger than that of the pure nonlinear material (PBZT in this case.)

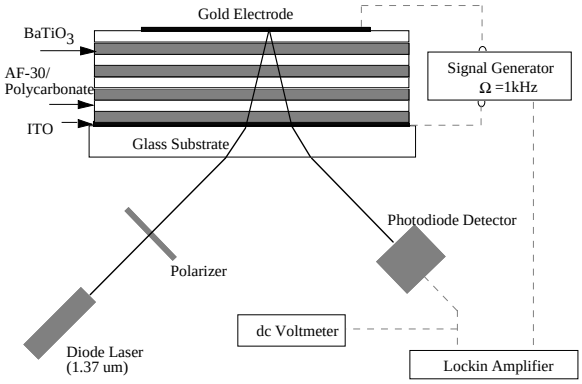

Figure 5: Sample geometry and experimental arrangement used to study an electrooptic composite material. The measure nonlinear response is 3.2 times that of the pure nonlinear material.

Enhanced Electrooptic Response. The enhancement achieved for the PBZT/titania composite was 35%. We have more recently fabricated a composite electrooptical material for which the measured enhancement [11] is a factor of 3.2. The material is illustrated in Fig. 5. It consists of alternating layers of rf-sputtered barium titanate and spin-coated polycarbonate containing a third-order nonlinear optical organic dopant. The effective nonlinear susceptibility of the composite describing the quadratic electrooptic effect was measured to have the value $3.2 + 0.2i \times 10^{-21}(\mathrm{m/V})^2$. The real part of this value is a factor of 3.2 times larger than that of the doped polycarbonate, which is the dominant electrooptic component of the composite. We have modeled the experiment both using effective medium theory and by solving the wave equation for our multilayered system, and we find that these approaches give consistent predictions which are in good agreement to the experimental results.

Bruggeman Geometry Composites. This geometry consists of two intermixed components possessing in general different linear and nonlinear optical properties. The linear optical properties are described by the equation

$$0 = f_a \epsilon_a \frac{\epsilon_a - \epsilon_{\mathrm{eff}}}{\epsilon_a + 2\epsilon_{\mathrm{eff}}} + f_b \epsilon_b \frac{\epsilon_b - \epsilon_{\mathrm{eff}}}{\epsilon_b + 2\epsilon_{\mathrm{eff}}} \tag{8}$$

which was derived initially by Bruggeman [8]. Alternative deviations have been devised by Landauer [12] and by Aspnes [13]. We have recently tested the prediction of Eq. (8) by measuring the refractive index of a material samples composed of porous glass (Corning Vycor)

containing one of several different nonlinear optical liquids: diiodomethane, carbon disulfide, carbon tetrachloride, and methanol. The porous Vycor glass has an average pore size of 4 nm and a 28% porosity. Results of this measurement are shown [14] in Fig. 6, along with the theoretical prediction of Eq. (8).

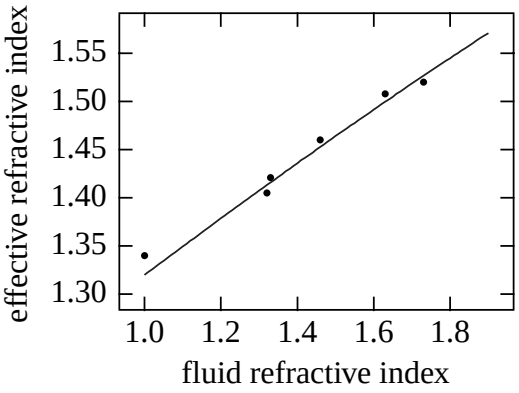

Figure 6: Measured linear refractive index of a composite material composed of a nonlinear liquid embedded in porous Vycor glass, plotted as a function of the liquid refractive index.

Strictly speaking, the nonlinear optical properties of a Bruggeman composite structure need to be described by a statistical theory, because by assumption the two constituents are randomly interspersed. As a simplifying assumption, one can assume that the field is spatially uniform within each component, leading to explicit predictions for the nonlinear optical response of such a composite. We have performed such a calculation [14] and found that under proper circumstances a modest enhancement of the nonlinear optical response is possible for a Bruggeman composite. We also performed measurements of the nonlinear optical response of Bruggeman composites and found that the predictions were in good agreement with the predictions of this theoretical model.

Maxwell Garnett Geometry Composites. We have performed [15] a study of the nonlinear optical response of an unusual nonlinear optical material consisting of gold nanoparticles suspended in a solution of the laser dye usually known as HITCI. This experimental study was designed to demonstrate a rather exotic consequence of local field effects. But constituents of the composite (i.e., both bulk gold and the dye solution) are reverse saturable absorbers, and hence the imaginary parts of their third order susceptibilities are both positive. Standard local field theory [16] predicts that the effective nonlinear susceptibility of the composite is given (for $f \ll 1$) by

$$\chi^{(3)}_{\rm eff} = fL^2|L|^2\chi^{(3)}_{\rm Au} + (1-f)\chi^{(3)}_{\rm dye\ sol'n} \tag{9}$$

where

$$L = \frac{3\epsilon_{\text{dye sol'n}}}{\epsilon_{\text{Au}} + 2\epsilon_{\text{dye sol'n}}}. \tag{10}$$

The linear dielectric constant of gold is negative and strongly frequency dependent. At a certain frequency, known as the surface plasmon frequency, the real part of the denominator of Eq. (10) vanishes. Under these circumstance, which corresponds to a laser wavelength of approximately 532 nm for our system, there is a large enhancement in the nonlinear optical response of the gold particles. In addition, the local field factor L becomes purely imaginary, and thus the product $L^2|L|^2$ becomes real and negative. Under these circumstance, this theory predicts that there will be a destructive cancellation of the two contributions to $\chi^{(3)}_{\text{eff}}$ in Eq. (9) even though both material contributions have the same sign. We have performed an experiment to test this counterintuitive prediction, and the results are shown in Fig. 7. These results are a striking confirmation of the importance of local field effects in establishing the nonlinear optical response of composite materials.

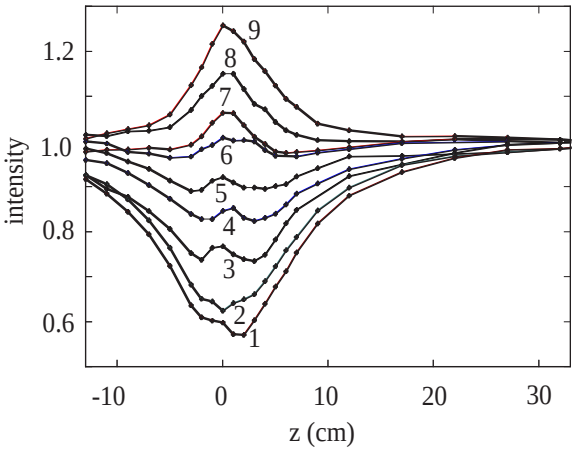

Figure 7: Z-scan results for the imaginary part of $\chi^{(3)}$ for a composite material consisting of gold nanoparticles suspended in a dye solution. The curves are numbered in order of increasing gold concentration. Note that curve 6, which refers to a gold fill fraction of 1.3×10^{-6}, shows a nearly complete cancellation between the two contributions to Im$\chi^{(3)}$.

Summary. We have summarized the results of an extensive research program aimed at quantifying the role played by local field effects in determining the nonlinear optical properties of optical materials. This work includes the first laboratory measurement of the Lorentz red shift, a direct consequence of local field effects which was first predicted by Lorentz in the late nineteenth century. We have also seem how local field effects can be used to enhance the response of nonlinear optical and electrooptic materials. In one particular instance, we were able to

construct a composite material in such a manner that its third-order susceptibility is 3.2 times larger than that of its more nonlinear component.

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